

EFFECT OF ACID ADDITION ON THE HYDROTHERMAL DECOMPOSITION OF CHITIN-DERIVED BIOMASS

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ABSTRACT

Hydrothermal decomposition of chitin-derived biomass was carried out using a batch tube reactor or fixed bed flow reactor at 300 - 400 °C for 30 - 120 sec under the pressure of 15 - 30 MPa, in order to clarify the influences of solvation by pressurized water and acid addition on the hydrolysis reactivity. HPLC and TOF-MS analyses of the WS fraction indicated that the decomposition at 300 °C provided oligomer products of 3 to 6 units with a low yield of ca. 5 %. On the other hand, the higher temperature above 350 °C produced the WS fraction with the yield as high as 30 %, however, a large amount of degraded products with UV adsorption was contained in WS, suggesting the ring skeleton of the unit structure as well as the ether linkage between the unit structure should be cleaved under the sub- and supercritical conditions. The addition of acetic acid or formic acid (5 or 10 %) accelerated very much the hydrolysis reaction of chitin to oligomers at the lower temperature of 300 °C, the conversion being increased up to ca. 70 %, although the WS fraction gained its weight by the acid addition. It is pointed out that the control of pH in the acid solution and the dissociation of the aggregate structure in the chitin polymer through the solvation are keys to the enhancement of the hydrothermal decomposition of chitin.

Keywords: Hydrothermal decomposition, acidic hydrolysis, chitin biomass

INTRODUCTION

Chitin, next to cellulose, is one of the major two biomass resources on earth.¹⁻³ Chitin is a natural 1,4-linked polymer which has N-acetyl group at the C-2 position, while the cellulose has hydroxyl group at the same position of the monomer unit. Although chitin and cellulose have the similar skeleton structure, their crystal structure and polymer chain characteristics are completely different depending upon their origins.^{4,5}

Hydrothermal treatments under the sub- or supercritical conditions have been reputed to be efficient for the selective decomposition of biomass.^{6,7} The supercritical water ($T_c = 374$ °C, $P_c = 22$ MPa) accelerates the decomposition of the polymers to produce valuable monomers and clean fuel by shorter reaction times of a few seconds.^{8,9}

In a previous study,¹⁰ it was reported that chitin was much less reactive than cellulose despite their similar unit skeleton structures, probably because their functional groups at C₂ differ (-NHCOCH₃ for chitin; -OH for cellulose), and their structural analyses before and after the hydrothermal treatment indicate that their intra- and intermolecular structures through hydrogen bonds may be the keys to their different hydrothermal reactivities. It was also revealed that the decomposition of chitin under the supercritical water conditions brought about black char materials with increased gas formation, indicating that the ring cleavage of the unit structure should take place above 350 °C, and the supercritical water condition be not favorable probably due to poor solvation of chitin.

In the present study, the effect of acid addition the hydrothermal decomposition reactivity of chitin-derived biomass was examined in order to moderate the reaction conditions for the selective production of chitin oligomers. At the same time, a flow type reactor with the fixed bed of chitin was also designed for the suppression of the secondary decomposition of water soluble fraction.

EXPERIMENTAL

Chitin powder of ca. 100 μ m particle size (deacetylation extent: 38 %) was supplied by courtesy of Japan Health Summit: JHS Co., Ltd. Acetic acid, formic acid of guaranteed grade and bamboo acid solution supplied from Asia Instrument Co.(extract from the carbonized bamboo) were used as additives for the hydrothermal treatment of chitin.

The reactor used for the hydrothermal reactions was a tube reactor (SUS 316, 9.3 mm i.d. X 83 mm length, 6 mL capacity) equipped with a thermocouple, a valve, and a pressure gauge. 0.5 g of chitin and 3.0 g of distilled water were charged into the reactor, and the atmosphere in the reactor was replaced with nitrogen or carbon dioxide gas. Then, the reactor was sealed after nitrogen gas was pressurized to the prescribed initial pressure.

The reactor was heated in two steps using two salt baths which were heated at 250 °C and the prescribed reaction temperature, respectively. The reactor was preheated at 250 °C for 3 min and subsequently heated in the second bath for the prescribed time while shaking at ca. 250 times a minute. The heating rates at the preheating to 250 °C and to the reaction temperature were ca. 100 °C/min and 600 °C/min. After the prescribed soaking time, the reactor was immediately cooled in a water bath to quench the reaction. The reaction conditions were described by both the heating time in the second heater and the final temperature reached during the reaction period. In the case of hot-water flow reactor with a fixed bed, 1 g of chitin was loaded in the cylindrical bed equipped with 5 μ m ceramic filters at both ends, the atmosphere in the reactor system was replaced with N₂ gas, and pressurized to 5 MPa N₂. The preheated water at the prescribed temperature in salt bath was flowed at 10 ml/min, and the extracted fraction(WS) by pressurized hot water was continuously recovered for sampling.

The liquid and solid contents in the reactor were thoroughly washed with water and filtered using No.4 glass filter. The water in the filtrate was distilled off under vacuum, and the water soluble (WS) fraction was recovered. The filter residue was washed with methanol to recover the methanol soluble (MS) and the insoluble (MI) fractions by the removal of methanol and the drying under vacuum. WS, MS, and MI fractions were weighed and each product yield was calculated based on the dry substrate base. The target product of oligomers was fractionated into WS fraction. MS (water insoluble but methanol soluble) fraction include the larger molecular weight products and degraded products such as aromatic and color compounds which are not able to be analyzed by HPLC. MI(insoluble fraction both in water and methanol) is the mixture of the unreacted substrate and char-like residue. Such characteristics were previously reported.^{6,7}

The WS fraction was analyzed by HPLC equipped with two columns(SEC W12 and SEC W13, Yokogawa Co.) and two detectors of UV(254 nm) and RI(refractive index) in series. HPLC was operated at 40 °C with 0.8 mL/min flow of a mixture of water and acetonitrile(70/30 by volume) as an eluting agent. TOF-MS of WS fraction was measured by MALDI(Matrix-assisted laser desorption ionization) method using Voyager of PerSeptive Biosystems.

RESULTS AND DISCUSSION

Decomposition of chitin in hot pressurized water

The conversion and product distributions in the hydrothermal reactions of chitin by a flow reactor are summarized in Table 1. At 350 °C, WS yields were 24.0 and 29.6 % under the reaction pressures of 7.0 and 18 MPa, respectively, being comparable to those obtained by a batch reactor as previously reported.¹⁰ It is marked that the secondary decomposition of WS was effectively suppressed by the flow reactor because WS was continuously extracted by hot water from the fixed bed reactor. A higher temperature of 400 °C at 25 MPa under the supercritical condition increased the WS yield to 35.5 %, while the recovery was lower because of the higher gas yield. In addition, the WI was converted to the black char above 350 °C, indicating that the retrogressive and coking reactions take place under the severer conditions.

Figure 1 shows the HPLC profiles of the WS fraction produced from chitin under the pressurized hydrothermal conditions. A standard sample of chitin oligomer obtained from JHS Co.Ltd. was also measured for comparison in Figure 1 (a), where monomer to pentamer are clearly shown in the chromatogram. The WS produced at 300 °C contained the oligomer products with 3 to 6 units, although the yield was as low as 5 %. The molecular weights of the oligomers were analyzed by MALDI TOF-MS as illustrated in Figure 2, where the corresponding trimer to hexamer were included in the WS. The WS produced at 350 and 400 °C contained a large amount of the degraded products with the adsorption by UV detector, indicating that the ring cleavage reaction of the unit structure should take place under the sub- and supercritical water conditions. The hydrolysis of chitin under the mild conditions is recommended for the selective production of the oligomers.

Effect of acid addition on the hydrothermal decomposition of chitin

Table 2 summarizes the hydrothermal conversion of chitin by a batch reactor with or without acid addition. The conversion to WS at 300 °C increased very much from 11.4 % in water to 22.0 % in bamboo acid solution(pH: ca. 3). A bamboo acid solution contains acids such as formic acid, acetic acid, and higher carbon acids. A higher temperature of 350 °C did not change the WS conversion with the higher gas yield.

5 % acetic acid aqueous solution significantly increased the WS yield to 55.5 % at 300 °C, and its 10 % solution further increased up to 73.7 % at 300 °C. The addition of 10 % formic acid gave a slightly higher WS yield of 76.3 % compared to that with 10 % acetic acid solution at the same temperature, although the some weight gains were observed with the addition of acetic or formic acid, suggesting some contribution of the addition reaction of the acid to the decomposed ether linkage between the unit structures of chitin.

Figure 3 illustrates the effect of pH on the WS conversion at 300 °C. The WS conversion linearly increased with pH, although it was saturated in the pH range between 1 and 2. The higher conversion is suggested to be related to the acidity of aqueous solution under the subcritical conditions. However, HPLC analyses of WS fractions indicated that the higher acidity may accelerate the ring cleavage of the unit structure and the addition reaction of acid.

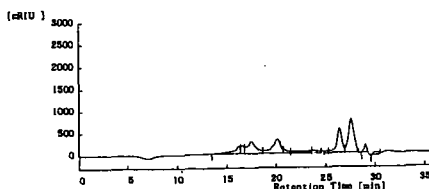
Based on the above results, it is pointed out that the control of pH in the acid solution and the dissociation of the aggregate structure in the chitin polymer through the solvation are keys to the enhancement of the hydrothermal decomposition of chitin.

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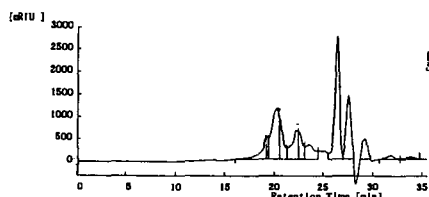
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Table 1 Hydrothermal decomposition of chitin by a fixed bed flow reactor

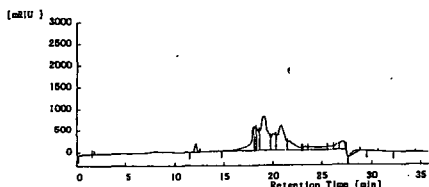
Salt bath temp.(°C)	Reaction press.(MPa)	WS Yield (wt%)	WI yield (wt%)	Recovery (%)
350	7.0	24.0	64.9	89.0
350	18.0	29.6	63.3	92.9
400	25.0	35.5	44.7	80.2



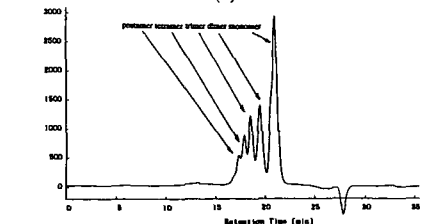
(d)



(c)



(b)



(a)

Fig. 1 HPLC profiles of the WS fractions produced under variable conditions

(a) standard chitin oligomers (b) 300 °C in water
(c) 350 °C in water (d) 300 °C in 5%CH₃COOH aq.

Table 2 Effect of acid addition on the hydrothermal decomposition of chitin by a batch tube reactor¹⁾

Additives (-)	Salt bath temp.(°C)	Reaction temp.(°C)	Yields (wt%)			
			WS	MS	MI	Gas
water	300	285	11.4	1.2	75.6	11.8
bamboo acid 100%	300	279	22.0	0.0	75.8	2.2
bamboo acid 100%	350	323	21.1	1.0	73.1	4.8
acetic acid 5 %	300	287	55.5	3.6	52.9	-
acetic acid 10 %	300	286	73.7	1.8	39.7	-
formic acid 10 %	300	288	76.3	0.4	29.2	-

1) reaction time 60 sec after the preheating at 250 °C for 3 min
chitin 0.5 g + solvent 3.0 g for water and bamboo acid,
chitin 0.4 g + solvent 2.4 g for acetic acid and formic acid solutions

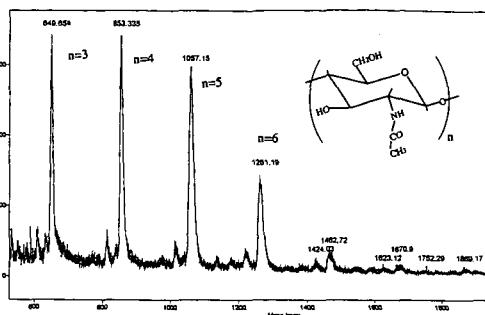


Fig. 2 TOF-MS profile of the WS fraction produced at 300 °C in water

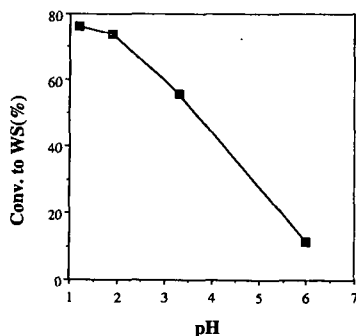


Fig. 3 Effect of pH on the conversion of chitin to WS

[pH; 10% formic acid 1.2
10% acetic acid 1.9
5% acetic acid 3.3
H₂O ca. 6]